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DEVOLATILIZATION OF COAL IN A TRANSPORT REACTOR

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INTRODUCTION

The objective of the Char Oil Energy Development (COED) project, sponsored by the Office of Coal Research, is to develop a process for conversion of coal to a pumpable mixture of char and oil. The work reported herein is part of the Project COED investigation. One approach to developing such a process involves the pyrolysis of coal using very high heating rates and very short residence times. Aside from reducing equipment costs, rapid pyrolysis is also desirable because volatile yields from coal are increased. In fact, under selected conditions, the quantity of material volatilized exceeds the ASTM volatile-matter content of the coal.

Systems most commonly employed to achieve the extremely rapid heating rates needed for maximum devolatilization--shock tubes, flash-heating apparatus and hot-strip microscopes--use such small samples that analysis and characterization of the products is difficult or uncertain. This drawback can be largely overcome by using a dispersed-phase transport reactor. With this system, larger quantities of coal can be heated for short periods at rates of more than 2500°C. per second.

EXPERIMENTAL AND RESULTS

The transport reactor, shown in Figure 1, is an externally heated tube through which coal is transported by means of an inert gas. Coal is charged from a hopper by means of a Syntron vibrator or a screw feeder. The coal is transported through the reactor by the carrier gas. The reactor is heated by a Globar-heated combustion furnace. On leaving the reactor, the bulk of the char is collected in a cyclone; the balance, in a settling vessel along with some tar. Tar mist and ultra-fine particles are collected on glass-wool filters. (These were found to be more effective than an electrostatic precipitator followed by dry ice-acetone and/or liquid nitrogen cold traps.) A cold trap after the filters collects moisture entrained in the gas, and the gas is metered and sampled for mass-spectrographic analysis.

Char collected after the cyclone is washed with acetone to remove condensed tar. The washed char is dried at 110°C. and is analyzed along with char from the cyclone. Acetone is evaporated from the acetone-solution of tar, and the weight of acetone-soluble tar determined. The respective amounts of solids and tars on the filters is determined by quinoline solubility.

Elkol coal, a sub-bituminous B coal from Wyoming was used in these studies. The analysis of this coal is shown in Table I.

TABLE I
Analysis of Elkol Coal
Elkol Mine
The Kemmerer Coal Company

<u>Proximate Analysis, wt. %</u>	<u>As-Received</u>	<u>Dry Basis</u>
Moisture	12.8	-
Volatile Matter	35.5	40.8
Fixed Carbon	47.6	54.5
Ash	4.1	4.7
<u>Ultimate Analysis, wt. %</u>		
Carbon		70.7
Hydrogen		5.4
Nitrogen		1.2
Sulfur		1.0
Oxygen		17.1
Ash		4.7

One of the objectives of this study was to volatilize a maximum amount of coal. From these studies, it was found that the two most important factors in the volatilization of coal were the carrier gas velocity and the furnace temperature.

The quantity of residual volatile matter in the product chars decreases as the carrier gas velocity, calculated at 22°C. and 1 atmosphere, is decreased from 20 to 4 feet per second. This decrease in gas velocity, shown in Figure 2, increases the calculated average residence time of coal in the 8-inch hot zone of the combustion furnace from about 8 to 40 milliseconds. All of these runs were made with the same coal feed rate and with a furnace temperature of 1100°C. The lowest volatile-matter content shown in this figure is about 6 times greater than that obtained when the same coal is heated in a fluidized bed at 1100°C. for 15 minutes. It is not known whether the relatively low devolatilization obtained in the transport reactor at 1100°C. results from insufficient time for devolatilization to be completed or from the char being quenched before it reaches the furnace temperature. Because of the difficulty in determining true char temperatures during devolatilization, all temperatures given herein are furnace temperatures.

Higher furnace temperatures cause increased devolatilization of coal, as shown in Figure 3. This is true for all carrier gas velocities shown in the figure. On the other hand, reducing the carrier gas velocity below 4 feet per second does not increase the amount of coal devolatilized. Because of heating limitations, temperatures above 1500°C. could not be attained with this system. It should be noted that char prepared at 1500°C. with a linear helium velocity of 4.0 feet per second still contains 2.7 percent of volatile components, as determined by the ASTM volatile-matter test.

The foregoing indicates that complete devolatilization of the coal cannot be obtained in the transport reactor when using cold helium as the carrier gas. In an attempt to add additional heat to the system, helium preheated to 550°C. was used as the carrier gas. A comparison of results obtained when using heated and unheated helium as carrier gases is shown in Figure 4. At 1100°C., the product char obtained with heated helium carrier gas contains about four percent less volatile material than that obtained with the cold helium, but the difference decreases at higher temperatures and virtually disappears at 1400°C. With heated helium also, no difference can be found in the amount of coal devolatilized when the linear helium velocity is reduced from 4.0 to 2.5 feet per second.

When steam is used in place of helium as a carrier gas, about 10 to 15 percent less devolatilization is observed. This is attributed to the higher specific heat and lower thermal conductivity of steam, as compared to helium.

Typical product yields obtained with glazed porcelain tubes at 1100 and 1300°C. are shown in Table II. Although more coal is devolatilized at 1300°C. than at 1100°C., as shown in Figure 3 and, in the volatile-matter and ash contents of the chars shown in Table II, more solids are produced at the higher temperature. The gas produced at 1300°C. contains less hydrocarbons than the gas formed at 1100°C. This suggests that volatile hydrocarbons are cracked at the higher temperature to form solids. Confirmation of the cracking reactions was obtained by isolation of vapor-cracked carbon from practically all of the runs made at 1300°C. and higher temperatures. This carbon accumulates in the coarse and fine fractions of the product chars on sieving, or it may be elutriated from the char in a fluidized bed.

Photos of vapor-cracked carbon are shown in Figures 5 and 6.

The quantity of vapor-cracked carbon formed in miscellaneous runs at 1300°C. is shown in Table III. After repeated use, porcelain tubes cause more cracking, as evidenced by the vapor-cracked carbon contents of Runs 89 and 93. The low vapor-cracked carbon content of the solids from Run 95 is attributed to the use of undried coal. Apparently coal moisture delays the temperature rise of coal particles. The high yield of carbon in Run 96 may be partly due to cracking of the hydrocarbons in the carrier medium which simulated a recycle gas.

TABLE II

Product Yields Obtained in Glazed Porcelain Reactors

100-x200-mesh Elkol Coal

Helium Carrier Gas Velocity, 4.0 ft./sec.

Run No.	88	97
Furnace Temperature, °C.	1100	1300
Feed Rate, gm./hr.	132	124
Coal Charged, gm.	111	62.2
<u>Coal Converted, %, dry basis</u>		
Char	50.1	55.3
Tar	3.6	1.8
Moisture	2.7	2.1
Gas	43.6	40.8
<u>Make-Gas Analysis, mol %</u>		
H ₂	22.5	49.0
CH ₄	18.2	7.7
C ₂ H ₂	4.3	7.2
C ₂	10.5	1.1
CO	35.4	28.6
CO ₂	7.5	6.0
C ₃ ⁺	0.7	0.3
<u>Char Analysis, %, dry basis</u>		
Volatile matter	15.6	5.6
Ash	4.6	6.4

TABLE III

Formation of Vapor-Cracked Carbon at 1300°C.

(Basis: Ash Balance)

Run No.	Solids Recovered, wt. %	Percent Vapor-Cracked Carbon	Corrected Char Yield, wt. %
89	46.0	4.8	41.2
93	52.0	14.6	37.4
95 ¹	50.5	6.9	43.6
96 ²	57.9	16.2	41.7

¹ Undried Elkol coal used.² Recycle gas used as carrier.

The most significant aspect of Table III, however, is that, if the solids recovery is corrected for the calculated carbon content, the corrected char yield is about 41 percent. This figure is considerably lower than the char yield obtained at 1100°C. Thus, it appears that on raising the furnace temperature from 1100°C. to 1300°C. the amount of coal volatilized is increased, but the effect is masked by the simultaneous production of vapor-cracked carbon.

If the true char yield of 1300°C. is 41 weight percent of the dried coal, then 59 percent of this coal must have been volatilized. This is far above the 41 percent indicated by the ASTM volatile-matter determination. Moreover, the char still contains about 6 percent volatile matter which can be removed. Thus, about 60 to 65 weight percent of this coal can probably be volatilized by rapid pyrolysis.

In order to reduce the secondary cracking reactions, the heating zone of the combustion furnace was shortened from 8 to 4 inches by changing the Globars. To get a temperature of 1100°C. with the shorter heating zone, it was necessary to preheat the carrier gas to about 450°C. Results obtained with the 4-inch Globars are presented in Table IV.

The total amount of volatile products produced at 1100°C. in these runs is about one-fourth lower than in Run 88, Table II, but the distribution is different. Thus, tar production is increased substantially and the yield of gas is decreased. The gas has a higher concentration of hydrocarbons and less hydrogen, indicating that less cracking occurs in the shorter hot zone. Also, the yield and volatile content of the chars are higher than from Run 88 shown in Table II, indicating less devolatilization of coal in the shorter heating period.

DISCUSSION OF RESULTS

The high yield of volatile material from the devolatilization of coal in the transport reactor is believed due to the extremely fast heating rates and the short residence times used. When coal is pyrolyzed, devolatilization and polymerization reactions occur simultaneously. The velocity of the polymerization reactions is slower than that of the devolatilization reactions; and in the short residence times employed in this dilute-phase reactor system, reaction products are quenched and recovered before extensive polymerization of reactive species can occur.

TABLE IV

Devolatilization with 4-inch Globar Heaters.
100-x200-mesh Elkol Coal
 Helium Carrier Gas Velocity, 4.0 ft./sec.

Run No.	80	81
Furnace Temperature, °C.	1100	1100
Feed Rate, gm./hr.	120	127.5
Total Coal Charged, gm.	50.1	53.3
<u>Coal Conversion, wt. %, dry basis</u>		
Char	57.1	60.0
Tar	10.6	9.3
Water	6.3	7.0
Gases	26.0	23.5
<u>Make-Gas Analysis, mol %</u>		
H ₂	15.9	17.4
CH ₄	17.9	17.5
C ₂ H ₂	1.2	0.6
C ₂	13.9	15.7
CO	37.8	33.6
CO ₂	9.9	12.4
C ₆ H ₆	0.4	0.3
C ₃	3.0	2.5
<u>Char Analysis, wt. %, dry basis</u>		
Volatile matter	20.5	21.9
Ash	4.2	4.8

TABLE V

Products Residence Times in Transport
and Fluidized-Bed Reactors

<u>Residence Time,</u> <u>seconds</u>	<u>Transport</u> <u>Reactor</u>	<u>Fluidized-Bed</u> <u>Reactor</u>
Gas	0.01-0.04	1-2
Solids	0.01-0.04	900

In Figure 2 it was shown that coal particles do not reach the indicated furnace temperatures, even at the lowest carrier gas velocities (or longest residence times) used. In order to estimate the temperature to which gases and solids were heated in the transport reactor, the char and gas analyses were compared with similar analyses obtained by devolatilizing this same coal in a 3-inch fluidized-bed reactor. This method of determining temperature is less rigid than might be desired, and the residence times of char in the two reactors is very different, as shown in Table V. Based on the analyses of products from the two reactors, the temperatures of the gas and char in the transport reactor were estimated to be about 300 and 500°C., respectively, below that of the furnace. These results are summarized in Table VI.

TABLE VI

Estimated Temperatures Inside Transport Reactor
Carrier Gas Velocity, 4.0 ft./sec.

Furnace Temperature, °C.	1100	1300
<u>Estimated Temperature, °C.</u>		
From hydrogen content of gas	775	980
From hydrocarbon content of gas	790	980
From VM of char	625	760

The lower char temperature probably results from ablation effects in which the rapid evolution of gases and tars lowers the temperature of the char particle. Similar, though less striking, results are reported by W. Peters¹ in devolatilization studies made with longer char residence times.

In summary, the transport reactor is effective for studying devolatilization of coal. Coal devolatilization reactions proceed very rapidly. With extremely short residence times, the amount of coal that can be volatilized is appreciably greater than that determined by the ASTM volatile-matter determination. Above 1100°C., formation of vapor-cracked carbon becomes extensive, probably due to cracking of tars and gases. Lastly, by varying the residence times within a hot zone, the distribution of products may be altered considerably.

ACKNOWLEDGMENTS

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¹ Peters, W., *Chemie-Ing-Techn.* 32 (3) 178 (1960).

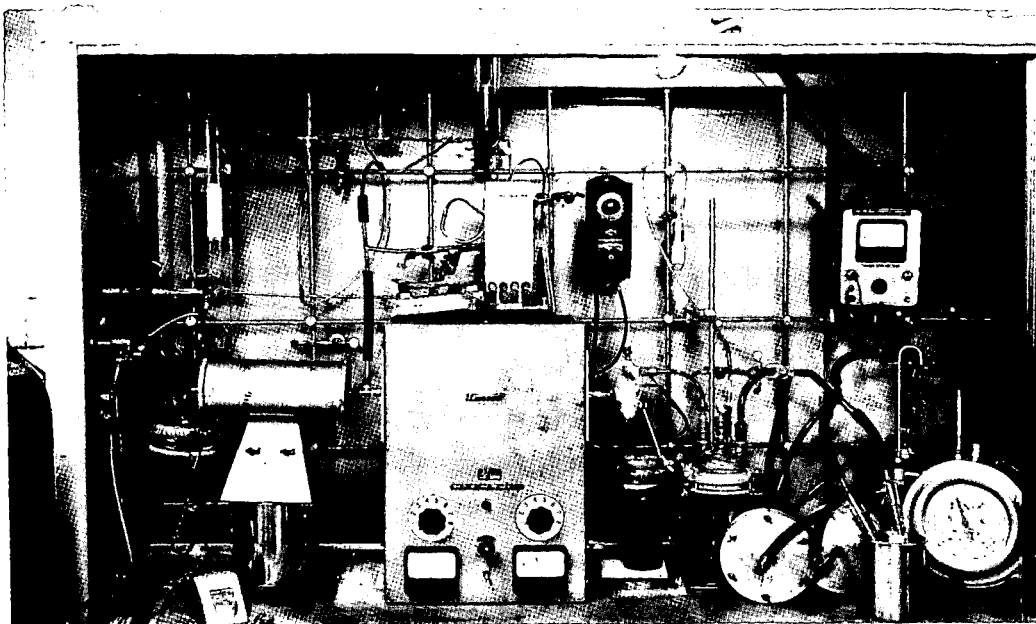


FIGURE 1
Transport Reactor Assembly

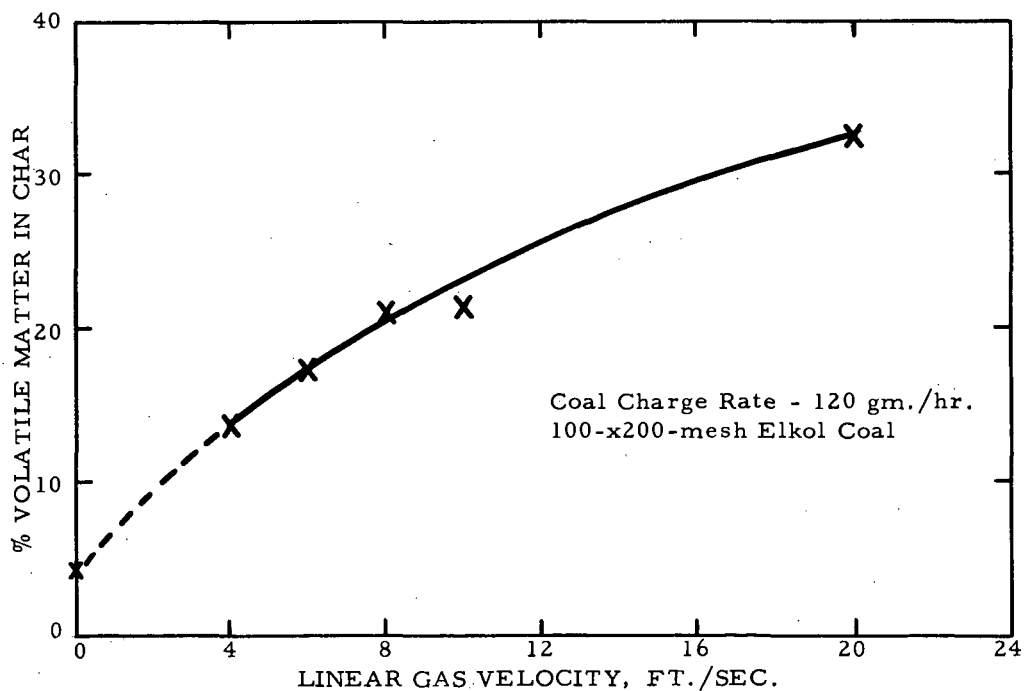


FIGURE 2
Effect of Carrier Gas Velocity on Coal Devolatilization
Furnace Temperature 1100°C.

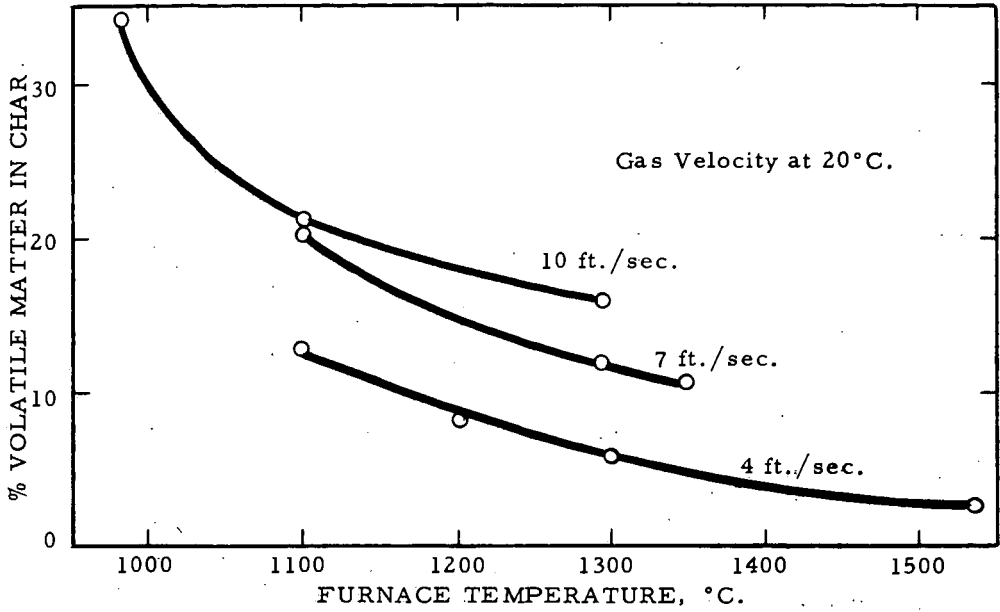


FIGURE 3
Effect of Furnace Temperature on Coal Devolatilization
Coal Charge Rate - 120 gm./hr.

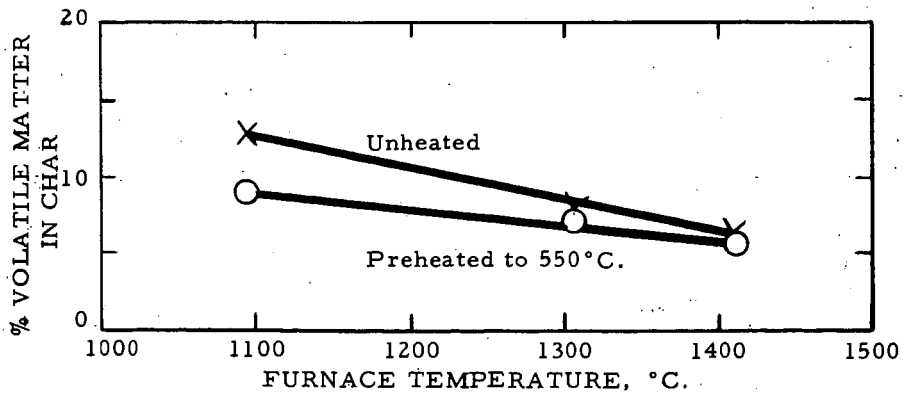
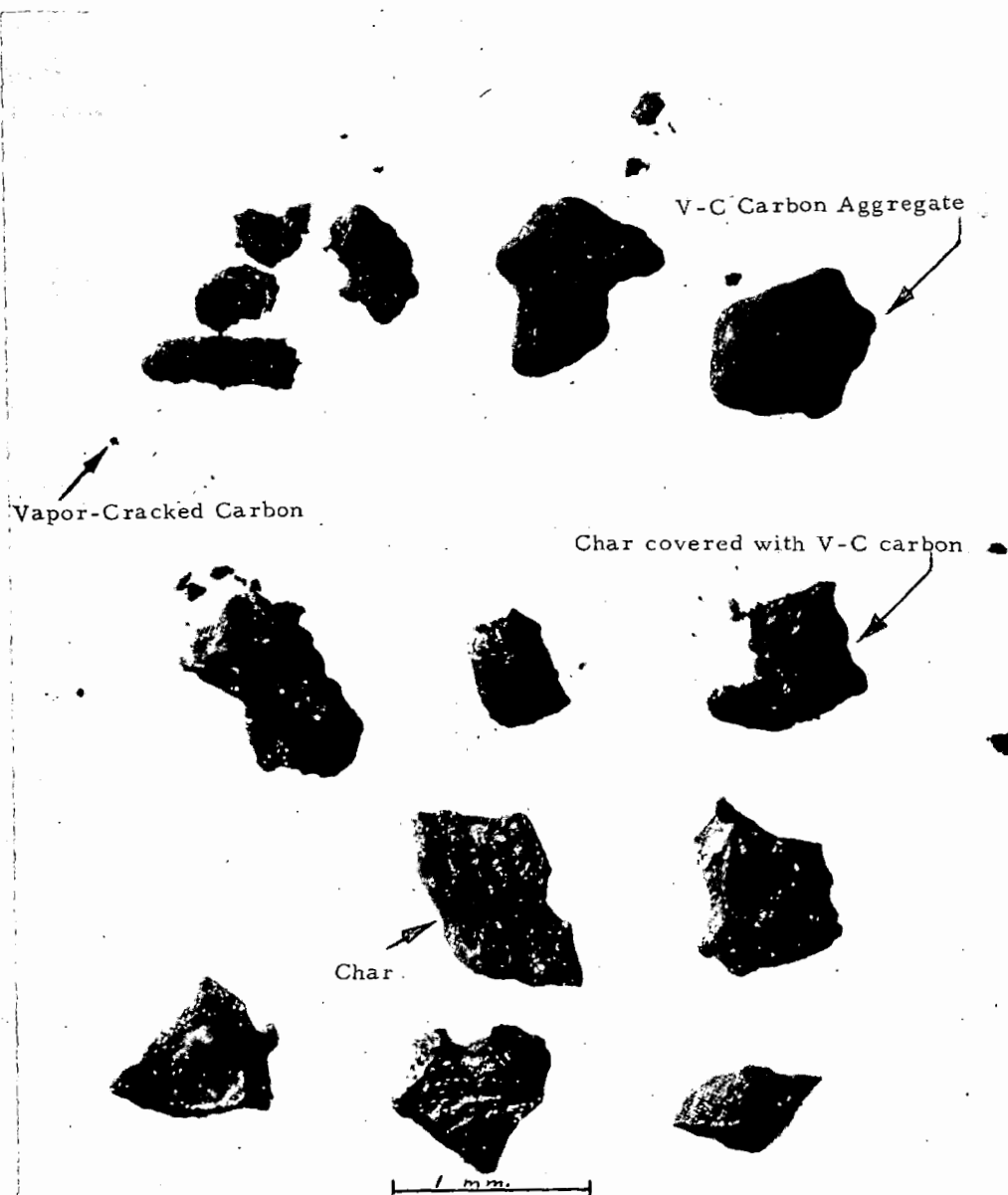


FIGURE 4
Effect of Carrier Gas Temperature on Devolatilization



Magnification 33 1/2 X

28-x48-mesh fraction collected in recovery section

Run conditions: 2400°F. Furnace Temperature

14-x60-mesh Elkol coal

4 ft./sec. He carrier gas

FIGURE 5

Vapor-Cracked Carbon in Coarse Fraction of Char

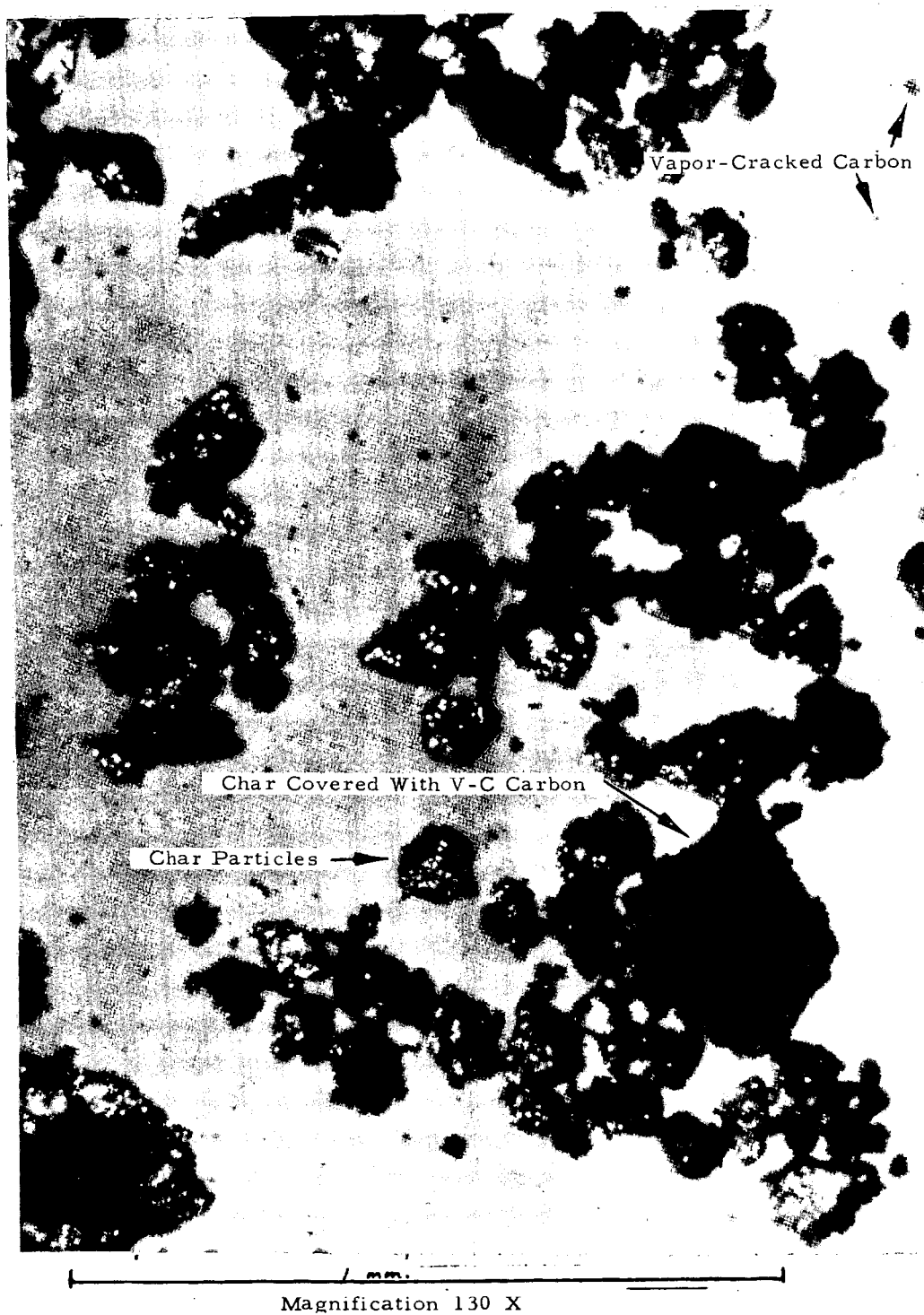


FIGURE 6
Vapor-Cracked Carbon in Elutriated Material